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(11) Publication number: **0 421 075 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: 90114314.9

(22) Date of filing: 26.07.90

(51) Int. Cl.5: C23C 16/02, C23C 16/40, H01L 21/285

(30) Priority: 27.09.89 US 413357

(43) Date of publication of application: 10.04.91 Bulletin 91/15

(84) Designated Contracting States: DE FR GB

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(54) Low pressure, low-temperature process for depositing silicondioxide.

(57) The present invention relates to a low-pressure chemical vapor deposition (LPCVD) process for depositing silicon dioxide. In particular, the present invention describes a process involving a pre-cleaning step in which all impurities are removed from the substrate followed by a LPCVD step performed at temperatures of between 200° C and 300° C.

More particularly, the present invention involves a process in which a substrate is washed using a predetermined cleaning process. The substrate is then exposed to a dilute hydrofluoric acid solution which removes native oxide and contaminants from the surface. Next, the substrate is rinsed with, for example, de-ionized water or ultra-clean water to remove any hydrofluoric acid or other residue from the previous process steps. A layer of semiconductor material, for example, silicon dioxide, is then deposited using a low-pressure chemical vapor deposition process in which the gas flow comprises silane, oxygen and nitrogen at temperatures below 300° C. Oxide qualities approaching those of thermally grown oxides have been achieved.

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LOW-PRESSURE, LOW-TEMPERATURE PROCESS FOR DEPOSITING SILICONDIOXIDE

The present invention relates, in general, to a high-throughput, low-pressure, low-temperature process for depositing high-quality silicon dioxide at temperatures of about 300° C or below.

In making integrated circuits for use in computers and other electronic devices, it is often desirable to deposit a thin layer of oxide material on a substrate. However, deposition of semiconductor materials by conventional techniques is frequently a lengthy process in which the ultimate quality of the deposited materials depends on a number of process parameters, some of which are difficult to control. Generally, conventional deposition processes comprise a pre-preparation step and a material deposition step.

Cleaning is important because it prepares the substrate surface for the subsequent material deposition step. If the substrate surface is not properly prepared, the interface between the substrate and the deposited material may include unwanted contaminates. In addition, if the substrate is not properly cleaned, the deposited material may not properly adhere to the substrate. Either of these conditions may result in undesirable electrical characteristics at the interface between the deposit and the substrate. The electrical and mechanical characteristics of the deposited material itself may also be detrimentally affected by deposition over an improperly cleaned surface. One conventional pre-oxidation cleaning technique is described in "Cleaning Solutions Based on Hydrogen Peroxide for Use in Silicon Semiconductor Technology," by Werner Kern and David Protinea RCA Review, June 1970, p. 187, which is hereby incorporated by reference.

The substrate over which the SiO_2 is to be deposited is typically a semiconductor material or passivation material and may include a number of materials at its surface, for example, where the SiO_2 is being deposited over a number of devices on an integrated circuit. In addition, the surface of the substrate may be uneven, including mesa structures, trenches and other variations.

The quality and characteristics of the deposited material are a function of the nature of the material deposition step in addition to the cleaning step. A number of techniques have been used in the art to deposit semiconductor material over a substrate, including chemical vapor deposition and plasma deposition. Each of these conventional techniques has advantages and disadvantages for the deposition of semiconductor materials. For example, plasma deposition techniques are useful for depositing high-quality oxides such as SiO_2 at low temperatures. Chemical vapor deposition (CVD), on the other hand, is useful for processing large numbers of wafers. However, CVD deposition normally requires extremely high temperatures to deposit high-quality oxides, while plasma techniques are normally not adaptable to processing large quantities of wafers.

A high-temperature (950° C) plasma-enhanced chemical vapor deposition process including a pre-treatment step is described in U.S. Patent 3,447,238 to Heynes et al . The pre-treatment described includes rinsing with a 10:1 solution of DI water and HF acid followed by a 10 minute hot (100° C) nitric acid treatment.

In U.S. Patent 3,486,951 to Morby et al. the oxide layer is formed by oxidation at 1100° C for 5 minutes. A high quality oxide is obtained by cleaning the wafer with a chromium trioxide and sulfuric acid solution, followed by a dip in a HF acid solution. Finally, the wafer is subjected to a nozzle spray of methyl alcohol and orthophosphoric acid.

"Low Pressure Chemical Vapor Deposited Oxide Process for MOS Device Application," Jack Lee and Chenming Hu, presented at the Symposium on VLSI Technology held in San Diego, May 10-13, 1988, describes a low-pressure chemical vapor deposition process (LPCVD) which operates at temperatures from 400 to 450° C. The process disclosed utilizes a densification step in nitrogen and a short annealing step in oxygen at 950° C.

The quality of a deposited oxide may be determined by measuring a number of "figures of merit". These figures of merit are electrical characteristics of the oxide which provide some indication of how an electronic device (e.g., an MOS field effect transistor) using that oxide will perform. Some of the more widely recognized figures of merit include breakdown voltage, interface trap density, oxide charge (flatband voltage) and interface minority carrier generation-lifetime.

Normally a high-quality oxide layer would have a breakdown field of greater than approximately 8.0 megavolts per centimeter (MV/cm). Further, a high-quality oxide layer would have a midgap interface trap density of less than approximately 4×10^{10} traps per electronVolt-centimeter squared ($eV\text{-}cm^2$). Finally, a high-quality oxide deposition would be expected to have an interface minority carrier generation-lifetime of more than approximately 40 microseconds in the silicon near the interface.

In depositing SiO_2 as in the present invention, it is known that conformality is also a figure of merit. Conformality is a measure of the degree to which the deposited oxide conforms to the surface of the substrate. It may be expressed as a ratio of the thickness of the deposited layer in a trench to

the thickness on a level surface. The thickness in the trench may be measured either at the mid-point, on the sidewalls or at the trench bottom. If the measurement is made at the trench mid-point, a conformality of 80% or better is desired. Tetraethylorthosilicate (TEOS) may be used to have a high degree of conformality, but introduces carbon and is therefore disadvantageous. Also, it is deposited at higher temperatures.

Oxides having acceptable figures of merit may be grown using high-temperature thermal oxidation. The process of growing oxides at high temperatures is a thermal process in which the oxide is grown by oxidation of the substrate, as opposed to chemical vapor deposition in which the oxide is deposited by a chemical reaction between the gas species (e.g., silane and oxygen) at the substrate surface. Thermal oxidation is disad vantageous in certain applications as the high temperatures required produce undesirable side effects such as junction migration and changes in implanted or diffused impurity profiles. High temperatures may also result in the introduction of unwanted defects or contaminants. In addition, some processing materials (e.g., aluminum) cannot tolerate high temperatures.

The drive toward low-temperature processing to produce smaller, shallower device structures has placed severe limitations on the formation of insulators in silicon technology. To overcome these limitations, researchers have recently begun investigating alternatives to high-temperature thermal oxides. Thus, it would be advantageous to provide a low-temperature (e.g., 200-300 °C) process for depositing high-quality SiO_2 films on a silicon substrate and achieving the quality of thermally grown SiO_2 films.

Other processes for depositing high-quality semiconductor materials at lower temperatures include plasma-enhanced chemical vapor deposition. Plasma deposition is a form of chemical vapor deposition in which a plasma is formed in the gas to enhance its deposition characteristics. These processes are normally low-throughput processes which are not readily adaptable to high volume manufacturing, resulting in a trade-off between oxide quality and manufacturability (i.e., cost). However, because the plasma must be in contact with each substrate, it is not possible to process more than a limited number of substrates and, thus, this is a very low-throughput process. Plasma deposition may also result in radiation damage to some sensitive materials. One such process is described by J. Batey and E. Tierney in "Low-Temperature Deposition of High Quality Silicon Dioxide by Plasma Enhanced Chemical Vapor Deposition," Journal of Applied Physics , 60 (9), November 1, 1986, at p. 3136.

Standard chemical vapor deposition is advantageous because it may be accomplished at temperatures well below the temperatures required for thermally deposited oxides, while retaining the high throughput of thermal deposition. However, conventional high-throughput chemical vapor deposition processes adapted to deposit oxides at low temperatures have not, to this point, proved capable of depositing thermal like high-quality oxides. (See, for example, Rosler Low Pressure CVD Production Process for Poly Nitride and Oxide , Solid State Technology, April 1977, pp. 63-70.)

It is known that oxides may be deposited by chemical vapor deposition (CVD) at low temperatures (e.g., in the 400-500 °C ranges. Oxides deposited by these low-temperature CVD techniques are well-known and are generally referred to as low-temperature oxides (LTO). The problem with these low-temperature oxides has been the low quality of the oxide compared with thermally grown oxides. To deposit SiO_2 by CVD from silane (SiH_4) and oxygen (O_2), a temperature of 450 °C or greater is generally required to achieve acceptable quality. However, even at these temperatures, the quality of deposited SiO_2 has not come close to the quality of thermally grown oxides.

The present invention relates to a low-pressure chemical vapor deposition (LPCVD) process for depositing silicon dioxide. In particular, the present invention concerns a process involving a pre-cleaning step in which impurities are removed from the substrate followed by a LPCVD step performed at temperatures which can be as low as between approximately 200 °C and 300 °C. Preferred processes of the present invention can be used to replace higher temperature LPCVD and thermal processes for depositing silicon dioxide.

More particularly, the present invention involves a pre-cleaning step in which a substrate is washed using a predetermined cleaning process (e.g., a pre-oxidation clean). The substrate is then dipped in a dilute hydrofluoric acid solution which removes native oxide and contaminants from the surface. Next, the substrate is rinsed with, for example, de-ionized water or ultra-clean water to remove any hydrofluoric acid or other residue from the previous process steps. Finally, a layer of silicon dioxide is deposited using a low-pressure chemical vapor deposition process in a gas flow which comprises silane, oxygen and nitrogen at temperatures of 300 °C or less.

Preferred embodiments of the present invention provide a process for depositing high-quality silicon dioxide at temperatures of approximately 300 °C or less.

The process of the present invention preferably provides for depositing high-quality silicon dioxide at temperatures below approximately 300 °C in a

13. A silicon dioxide layer deposited by low pressure chemical vapor deposition at a temperature of between 200 and 300 °C having the following properties:
an etch rate of approximately 145 nm (1450 Å) per minute in a buffered oxide etchant;
a midgap interface trap density (D_{it}) of less than approximately 5×10^{10} interface states per $eV\text{-}cm^2$;
a minority carrier lifetime in the substrate of more than 40 microseconds; and
a breakdown field strength of greater than 8 megavolts per centimeter.

14. A silicon dioxide layer according to claim 13 wherein said buffered oxide etchant comprises:
a solution of approximately nine parts saturated ammonium fluoride in water to approximately one part hydrofluoric acid.

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EUROPEAN SEARCH REPORT

Application Number

EP 90 11 4314

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EXTENDED ABSTRACTS, vol. 82-1, May 1982, pages 102-103, abstract no. 64, Pennington, NJ, US; P.K. BOYER et al.: "Laser photodeposition of silicon oxides and silicon nitrides" * Page 102, column 1, lines 15-33,37-40; table 1 * – – –	1,2,5, 8-13	C 23 C 16/02 C 23 C 16/40 H 01 L 21/285
A	J. ELECTROCHEM. SOC.: SOLID-STATE SCIENCE AND TECHNOLOGY, vol. 130, no. 9, September 1983, pages 1888-1893, Manchester, NH, US; C. COBIANU et al.: "A theoretical study of the low-temperature chemical vapor deposition of SiO2 films" * Page 1888, abstract, column 2, lines 16-21 * – – –	1,4-6,12, 13	
A	20TH ANNUAL PROCEEDINGS RELIABILITY PHYSICS, San Diego, CA, March-April 1982, pages 244-248, IEEE catalog no. 82CH1727-7, New York, US; J.R. MONKOWSKI et al.: "Failure mechanism in MOS gates resulting from particulate contamination" * Page 244, table 1 * – – –	1,3,4,7,12	
A	JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 121, no. 8, August 1974, pages 1103-1107, Manchester, NH, US; Y. AVIGAL et al.: "A new method for chemical vapor deposition of silicon dioxide" * Page 1104, column 2, lines 43-44; page 1105, column 1, lines 1-5; table 2 * – – –	14	**TECHNICAL FIELDS SEARCHED (Int. Cl.5)** C 23 C H 01 L
A	IEEE TRANSACTIONS ON SEMICONDUCTOR MANUFACTURING, vol. 2, no. 3, August 1989, pages 69-75, New York, US; H. MISHIMA et al.: "Particle-free wafer cleaning and drying technology" * Page 70, column 1, lines 7-21 * – – – -/-	3	

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	21 January 91	EKHULT H.U.

CATEGORY OF CITED DOCUMENTS

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E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

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EUROPEAN SEARCH REPORT

Application Number

EP 90 11 4314

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 134, no. 4, April 1987, pages 1031-1033, Manchester, NH, US; G. GOULD et al.: "The influence of silicon surface cleaning procedures on silicon oxidation" * Page 1031, column 1, lines 46-65 *	3	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	21 January 91	EKHULT H.U.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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A: technological background
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E: earlier patent document, but published on, or after the filing date
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L: document cited for other reasons

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